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Vibrational spectra and assignments of 1 hydroxy, 2 hydroxy and 2, 6 dihydroxy naphthols

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The infrared absorption spectra of 1- & 2-naphthols and 2, 6 dihydroxynaphthalene have been recorded in the frequency range 200-4000 cm^{-1} using different infrared spectrophotometers. Vibrational assignments have been given for all the observed frequencies by assuming C_s symmetry in case of 1- and 2-naphtols and C_{2h} in case 2, 6-dihydroxy naphthalene. The study conforms the assignment of many prominent skeletal vibration of naphthalene and shows the effect of single substitution as well as a highly symmetric disubstitution. The appearance of 315 cm^{-1} substituent characteristic frequency shows that 2-naphthol is a well behaved molecule contrary to the observations made by earlier workers

1. INTRODUCTION

Luther and Gunzler (1955) have measured the infrared frequencies of a number of substituted naphthalenes along with 1- and 2-naphthols and Singh & Singh (1970) have reported the I.R. spectra of these two molecule in the frequency range 700-4500 cm^{-1}. Soda (1961) has given a tentative assignment for the infrared frequencies of 1-naphthol by correlating them with those of phenol and p-tert-butuyl phenol. These studies were, however, confined to selective features of the spectra and to the discussion of a few modes of vibrations only. More so these studies were highly restricted due to the ambiguities in the vibrational assignment of the parent molecule. A large amount of literature is now available on the vibrational frequencies of naphthalene. The recent studies of phosphorescence spectrum of naphthalene by Hanson (1969), Raman scattering tensors for single crystals of naphthalene by Hanson & Gee (1969) and high resolution studies by Hollas (1962) have resulted in a definitive assignments of some modes of naphthalene which were a point of controversy for earlier workers.

In the present investigation the I.R. spectra of 1- and 2-naphthols and 2, 6-dihydroxynaphthalne in the frequency range 200-4000 cm^{-1} have been

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recorded. The vibrational assignments have been given for most of the fundamental modes using the Raman data published by earlier workers (Luther 1962).

2. Experimental

All the three compounds were Fluka made pure quality, supplied by J. Kundan & Co. Bombay. The infrared spectra of the compounds were recorded on 621-Perkin Elmer infrared spectrophotometer by taking the samples in the form of powdered solids mixed with potasium bromide and pressed into pellets.

3. Analysis and Discussion

If the substituent OH is treated as single particle, the molecule 2, 6-dihydroxy-naphthalene belong to C_{2h} point group and the two molecules 1- and 2-naphthols belong to C_s point group, with the molecular plane as the only element of symmetry.

The reduction of various symmetry species of D_{2h} point group into those of C_{2h} and C_s point groups is shown in table 1. The assignmnt of various frequencies to different modes have been made on the basis of intensity considerations and by correlating these with each other and with those of naphthalene and other substituted naphthalenes, benzene and phenol.

Table 1. Resolution of various point groups under D_{2h} symmetry

Species of D_{2h}	Resolved into	
	Species of C_{2h}	Species of C_s
a_g (R)	a_g (R)	a'(I.R., R)
b_{1g} (R)		
b_{2g} (R)	b_g (R)	a''(I.R., R)
b_{3g} (R)		
a_u (X)	a_u (I.R.)	
b_{1u} (I.R.)		
b_{2u} (I.R.)	b_u (I.R.)	
b_{3u} (I.R.)		

I.R.—Infrared active.
R - Raman active.
X —Inactive.

The normal modes of vibrations in all the three molecules may be classified into two categories :

(1) Vibrations involving the carbon and hydrogen atoms;

(2) Substituent characteristic vibrations.

(I) Naphthalene like vibrations :

The frequency of 712 cm^{-1} appearing strongly in the I.R. as well as Raman spectrum of 1-naphthol has been assigned to ring breathing frequency corresponding to 763 cm^{-1} a -vibration of naphthalene. This has also been observed strongly in I.R and Raman spectrum of 2-naphthol at 770 cm^{-1}. The slight increase in its value in case of β-substitution and large reduction in case af α-substitution is in congormity with the theoretical calculations of Luther (1948). The vibrational spectra of a number of mono-substituted naphthalenes, reported earlier, also favour the present assignment. In I.R. spectrum of 2, 6-dihydroxynaphalene no frequency corresponding to this mode has been observd which is in conformity with th selection rules for the C_{2h} point group.

The fundamentals appearing strongly at 1377 cm^{-1} in Raman spectrum of 1-naphthol and at 1384 cm^{-1} in both I.R. and Raman spectra of 2-naphthol have been assigned as C—C stretching mode corresponding to 1379 cm^{-1} a_g -type vibration of naphthalene. This is again absent in I.R. spectrum of 2, 6-dihydroxy-naphthalene as theoretically expected.

The inplane angle deformation frequencies α (CCC), may be modified in form and become X-sensitive in substituted naphthalenes. The present study shows that the frequencies corresponding to these modes are generally reduced on substitution. The frequency corresponding to 506 cm^{-1} b_{1g} type vibration of naphthalene is observed with the intense bands at 482 cm^{-1} in both 1- and 2-naphthols. Similarly, the frequencies corresponding to 512 cm^{-1} a_g - and 618 cm^{-1} b_{3u} -type vibrations of naphthalene are slightly increased in 1 and 2-naphthols. These features may be attributed to X-sensitivity of the corresponding modes.

The frequencies appearing strongly at 1455 cm^{-1} and 1471 cm^{-1} in both I.R. and Raman spectra of 1- & 2-naphthols respectively are correlated to 1460 cm^{-1} a_g -type vibration of naphthalene. Due to the strong appearance of these frequencies and the corresponding frequencies in other mono-substituted naphthalenes, we take 1460 cm^{-1} vibration of naphthalene as fundamental one, contrary to the assignments given by Mitra & Bernstein (1959) and Lippincott & O'Reilly (1955). The same is, however, in agreement with the assignments given by Hollas (1962) and Luther *et al* (1962).

(II) Substituent characteristic vibrations :

In phenols and similar compounds the C–O stretching mode, under the influence of the ring, appars at higher frequencies than the planer O–H deformation vibration. There, are therefore, possibilities of coupling between β(OH) and ν(CO) frequencies or between the latter and the aromatic ring vibrations. During the present course of investigation we have observed two strong bands at 1280 and 1310 cm $^{-1}$; 1280 and 1325 cm^{-1}; 1280 and 1320 cm^{-1} in 1-, 2- and 2, 6-dihydroxy compounds respectively. The higher of the two is assigned as C–O stretching mode and the lower one as O–H deformation mode. In case of 2, 6-dihydroxy molecule, there is another ν(CO) vibration, which appears very strongly at 1425 cm $^{-1}$ is correlated to 3056 cm^{-1} b_{2u} -type vibration of naphthalene.

Table 2. Vibrational assignments of 1- & 2-naphthols and 2, 6-dihydroxy-naphthalene

Fundamentals of naphthalene	1-naphthol		2-naphthol		2, 6-dihydroxy naphthalene	Probable mode of vibration
	I.R	Raman	I R	Raman	I R	
176 b_{1u}	-	184(30)	—	173(28)	--	Φ(CC)
213 au	—	—	-	225(14)	--	Φ(CC)
285 b_{3g}	—	271(20)	—	-	--	Φ(CC)
362 b_{2u}	350(15)	--	350(21)	350(14)	353(3)	α(CCC)
392 b_{2g}	390(sh)	—	—	391(28)	—	Φ(CC)
468 b_{3g}	460(15)		445(50)	--	--	Φ(CC)
478 b_{u}	478(45)	471(60b)	470(77)	466(42)	470(30)	Φ(CC)
506 b_{1g}	482(50)	—	482(90)	—	—	α(CCC)
512 a_{g}	520(30)	528(40)	520(40)	527(56)	--	α(CCC)
575 a_{u}	570(80)	574(50)	--	573(28)	570(65)	Φ(CC)
618 b_{3u}	630(45)	627(10)	626(64)	—	610(30)	α(CCC)
727 b_{2g}	—	—	715(64)	—	695(40)	γ(CH)
763 a_{g}	710(80)	713(70)	770(50)	769(70)	—	ν(CC)
772 b_{3g}	770(sh)	—	753(70)	—	—	γ(CH)
780 b_{1u}	—	782(30)	—	782(42)	740(10)	γ(CH)
810 b_{2u}	790(95)	—	812(85)	—	820(50)	α(CCC)
860 a_{u}	860(65)	—	868(sh)	—	860(95)	γ(CH)
938 b_{1g}	—	923(0)	908(73)	--	—	α(CCC)
950 b_{2g}	578(50)	—	585(45)	—	590(65)	γ(CX)
955 b_{1u}	950(30)	—	949(sh)	—	950(100)	γ(CH)
965 a_{u}	960(40)	—	960(75)	—	962(40)	γ(CH)
983 b_{3g}	980(sh)	—	985(20)	985(28)	—	γ(CH)

Table 2 (*Contd.*)

Fundamentals of naphthalene	1-naphthol		2-naphthol		2, 6-dihydroxy naphthalene	Probable mode of vibration
	I.R	Raman	I.R.	Raman	I.R.	
1008 b_{3u}	1048(80	—	—	1063(14)	—	α(CCC)
1025 a_g	1020(80)	1020(20)	1015(24)	1015(28)	—	ν(CC)
1125 b_{2u}	1085(90)	1083(40)	1120(48)	1119(0)	1120(80)	β(CH)
1135 b_{3u}	878(86)	879(50)	880(70)	885(28)	870(90)	β(CX)
1144 a_g	—	1141(40)	1140(50)	—	—	β(CH)
1168 b_{1g}	1150(60)	—	1175(70)	1177(14)	-	β(CH)
1212 b_{3u}	1210(50)	—	—	—	1230(95)	β(CH)
1240 b_{1g}	1240(80)	1246(30)	1242(60)	1238(14)	-	β(CH)
1265 b_{2u}	1270(90)	—	—	—	1270(70)	β(CH)
1365 b_{3u}	1362(80)	—	1360(41)	—	1370(40)	ν(CC)
1379 a_g	—	1377(10b)	1382(54)	1380(100)	—	ν(CC)
1389 b_{2u}	1390(90)	—	—	—	1390(80)	ν(CC)
1436 b_{1g}	1440(sh)	—	1410(60)	—	—	ν(CC)
1460 a_g	1455(50)	1455(60)	1470(70)	1473(53)	—	β(CH)
1504 b_{3u}	1510(30)	—	1515(53)	—	1520(95)	ν(CC)
1579 a_g	1580(80)	1577(70)	1585(50)	1579(42)	—	ν(CC)
1595 b_{2u}	1600(80)	—	1603(58)	—	1610(100)	ν(CC)
1624 b_{1g}	1630(30)	—	1630(55)	—	—	ν(CC)
2968 b_{2u}	—	—	—	—	2870(30)	ν(CH)
2980 b_{1g}	—	—	—	-	—	ν(CH)
3025 b_{1g}	—	—	—	-	—	ν(CH)
3004 a_g	—	—	—	—	-	ν(CH)
3029 b_{3u}	—	—		—	3040(40)	ν(CH)
3055 a_g	3050(80)	—	3060(80)	-	—	ν(CH)
3056 b_{2u}	—	—	—	—	1425(70)	ν(CX)
3085 b_{3u}	1310(70)	—	1325(30)	—	1320(30)	ν(CX)
	3230(100)	—	3230(100)	—	3280(100)	ν(OH)
	1280(sh)	—	1280(70)	—	1280(60) 1152(90)	β(OH)
	330(15)	—	315(27)	—	325(10)	γ(OH)

Note 1. Numerals in parantheses indicate the relative intensity of the corresponding band

2. The notations ν, α, β and γ denote bond stretching, angle deformation, in-plane bending and out of plane bending on twist of the bonds on angles

The O–H stretching frequency in case of phenols varies from 3220-5656 cm^{-1} depending upon the various states of the compound (Bellamy & Pace 1966). In the present case strong bands appearing at 3230 cm^{-1} in both 1- and 2-naphthols and at 3280 cm^{-1} in 2, 6-dihydroxy compound have been taken as ν(OH) vibrations.

The frequencies appearing vary strongly at 878, 883 and 870 cm^{-1} in 1-, 2-, and 2, 6-dihydroxy comounds respectively are taken to be β(CX) vibrations. The frequencies observed at 330, 315 and 325 cm^{-1} in 1-, 2-, and 2, 6-dihydroxy compounds respectively are assigned as an out of plane OH vibration (OH–torsion). The assignment of 315 cm^{-1} frequency in case of 2-naphthol as substituent characteristic vibration is in conformity with its behaviour in the electronic spectra (Sharma & Singh 1976), where it appears very strongly as a fundamental and also gives rise to a parallel series of bands. In the absence of this frequency, 2-naphthol was earlier reported (Singh & Singh 1965) as behaving abnormally in the electronic spectra.

Other frequencies observed and assigned as fundamentals are shown in table 2.

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